June 14, 1962

Progress Report No. 2
Project 1158-5

Dear Sam:

We believe a second report is due to you at this time in order to bring the status of the research up to date. For completeness, we have gone into quite a bit of detail in the x-ray diffraction technique, the camera, and the methods by which the samples were prepared so that a working knowledge could be provided should there be a desire to have similar work done in your laboratory at a future date. The reproduction of the x-ray diffraction patterns are direct contact positives from the original x-ray diffraction patterns and are actual size. The program is proceeding according to plan, but we are continuously seeking ways and means of decreasing the sample size and increasing the sensitivity. We are also planning to make densitometric measurements from the x-ray diffraction patterns and to reduce the data to correspond to the ASTM x-ray diffraction card index. After the things mentioned above have been accomplished, we should be able to do samples other than standards. After reading the things we are reporting, we would appreciate your criticism as to the progress of the program and the results.

X-Ray Diffraction Techniques

When x-rays impinge upon matter, a portion of the x-rays is scattered by the atoms of the substance. If the atoms are arranged in an orderly manner, that is, if the substance is crystalline, then the scattered rays from different

1 Copy to SAB (Jun)
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atoms will cancel and reinforce each other in a regular pattern. In the usual diffraction experiment, the x-ray beam is collimated into a narrow pencil by pinholes in lead (see Fig. 1). The narrow beam then traverses the sample of crystalline material. The sample may be a single crystal, or, as pictured in Figure 1, a powder made up of tiny crystalline granules. The scattered or diffracted x-rays strike a photographic film. If the sample is a single crystal aligned with one of the principal axes parallel to the collimated x-ray beam, then the diffraction pattern recorded by the film will be a system of spots or streaks symmetrically distributed about the point of intersection of the undeviated beam with the film. For practical reasons, the direct beam of x-rays is not allowed to strike the film. The exposure produced by the direct beam and the fluorescent x-rays from silver, bromine, and iodine atoms would be spread over a large fraction of the central portion of the film. The direct beam is stopped by a lead cup or allowed to pass cleanly through a hole punched in the film. When the sample is powdered, the random orientation of the crystalline granules produces a series of concentric rings on the photographic film. If the powder is uniform and of the proper grain size, the rings will be of uniform intensity and width. If the powder contains granules considerably larger than the average, then there will be spots or streaks mixed in with the rings. If the powder is too fine, the rings will be weak and diffuse and may disappear altogether.

The interpretation of the diffraction pattern may be accomplished with the aid of Figure 2. The small circles represent a series of atoms in planes of spacing, d. The planes make an angle θ with the incident x-rays, lines AB and DF. It has been found experimentally that the diffracted x-ray beam behaves as though the x-rays are reflected from a plane mirror, but only at certain angles.[1] Consider, then, the scattered x-ray beam defined by lines BC and FH also making an angle θ with the atomic planes. Thus the diffracted ray makes an angle 2θ with the incident ray. Note that the ray DFH is longer than ABC by the amount of EFG. That is, the point H lags behind point C by the distance EFG. The waves at points C and H, however, will be in phase and reinforce each other if EFG is an integral number, n, of x-ray wavelengths, λ. That is,

$$n\lambda = EFG.$$

Now $EF = FG = BF \sin\theta$, but $BF = d$, the atomic plane spacing. Thus, $n\lambda = 2d \sin\theta$. This is the Bragg law of x-ray diffraction.[1,2] The angle θ may be determined from the distance, r, of the diffraction spot or ring from the central point and D, the distance from the sample to the film (Fig. 1). In

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1 Clark, G. L., Applied X-Rays, McGraw-Hill, New York, 1955, pp. 95 - 102.

2 Azaroff, L. V., Norelco Reporter, Vol. VI, Nos. 4 - 5, pp. 76 - 79.

powder diffraction patterns, the diameter of the rings (2r) is readily measured. Distance D is most accurately determined by mixing some material of known atomic spacing, d, with the unknown.

The wavelength λ is determined by the anode or target material in the x-ray tube. Copper is a very widely used material for diffraction experiments. The radiation from a copper target is diagrammed in Figure 3.[2,3] The characteristic copper radiations, $K\alpha$ and $K\beta$, are superimposed on a continuous background radiation. To avoid a multiplicity of spots or rings arising from all the different wavelengths present in the output of the x-ray tube, it would be desirable to limit the x-rays to the $K\alpha$ wavelength. This is accomplished readily for a copper target tube by placing a thin sheet of nickel between the x-ray tube and the pinhole collimator (Fig. 1). The absorption of nickel is represented by the dashed curve of Figure 3. Thus the $K\beta$ and the shorter continuous wavelengths from copper are greatly attenuated with respect to the $K\alpha$ radiation. In general, a filter of one atomic number less than the atomic number of the x-ray target material will limit the radiation to the $K\alpha$ wavelength region.

In this laboratory, the source of x-rays for diffraction studies is a General Electric Type CA-7 copper target tube. This tube is mounted horizontally above a spectrogoniometer circle on a G.E. Type XRD-5 table. The x-ray tube window opposite the spectrogoniometer faces a camera track. The

[3] Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1953, pp. 2399 and 2406.

tube is powered by the G. E. Type XRD-5 high-voltage supply. This supply provides up to 50 kilovolts peak at 50 milliamperes. The Type CA-7 tube is limited to 35 kv and 16 ma. The XRD-5 power supply provides continuous voltage adjustment and four preset current adjustments. A Philips Micro Camera[4] was purchased by this project. Figure 4 shows this camera in position next to the x-ray tube. This camera consists of an airtight cylindrical body (No. 8 in Fig. 4), which may be evacuated or filled with hydrogen or helium when required. The front of the body is removable and secured to the rest of the body by a threaded clamping ring (No. 9 of Fig. 4). The pinhole collimator (No. 2 of Fig. 4) is held in a hole by the threaded retainer (No. 1 of Fig. 4). Thus, collimators may be changed readily. A nickel foil filter is usually taped over the hole in the collimator retainer. The sample support is carried on the inner side of the camera front (No. 3 of Fig. 4). The sample support may be moved laterally to center the sample with the axis of the pinholes. The film (No. 5 of Fig. 4) is held by a clip to the film support (No. 6 of Fig. 4) which plugs into a socket in the camera body. A fluorescent screen backed by lead glass (No. 7 of Fig. 4) is provided for precise alignment of the pinholes with the x-ray beam. The assembled camera is held in a holder clamped to the camera track on the XRD-5 table. The camera may be removed

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[4] Bergmann, M. E., Norelco Reporter, Vol. VI, Nos. 4 - 5, pp. 96 - 100.

from and replaced in the holder without disturbing the alignment. To insert a sample, the camera is removed from the holder and opened at the locking ring. The powdered samples are packed in small washers (No. 4 of Fig. 4). These washers are 0.25 in. outside diameter and have holes ranging from 0.35 to 1.0 mm diameter. The holes are funnel-shaped on one side to facilitate filling. The entire front of the camera is placed on the stage of a microscope with the sample holder up. The camera front is positioned so that the pinholes are centered in the cross hairs of the microscope ocular. The filled sample washer is put in place, and the holder is moved with respect to the camera front to align the sample with the cross hairs. Thus the sample is on the axis of the pinhole collimator. The camera is carried into a darkroom for loading with a film. The size of film required is about 35 by 40 mm. We have used both double-coated industrial x-ray film and single emulsion dental film. The dental films are already to size. A hole is punched in the film with a punch supplied with the camera. The film is clipped to the film support with the hole in the film centered on the hole in the support. The support is plugged in place and the front secured by the clamp ring. The camera is now ready for placement in the holder next to the x-ray tube.

Diffraction Patterns

Figures 5, 6, and 7 are contact prints of actual diffraction patterns made in the Philips Micro Camera. All these patterns were obtained using 0.35 mm pinholes. The film to sample distance was 15 mm. Films were developed for 2 - 4 minutes in G. E. Supermix x-ray developer. Most of the patterns were recorded on Rinn DC-1, No. 2 size, dental x-ray film with an exposure of 1/4 to 1 hour. The black dot in the center of each pattern is produced by the hole punched in each film.

The differences in diffraction patterns from the different compounds is quite strikingly illustrated by Figure 5. Even for patterns 4, 7, and 9, where the only difference in compounds is in the metal chelated by disodium ethylene diamine tetraacetate (EDTA). Plain Na_2 EDTA is represented by pattern No. 8. The effect of a relatively heavy metal, zinc, is shown by the broad exposed area in the center of No. 7. To some extent, the iron in hemin, pattern No. 3, produces also a broad central exposure. Pattern No. 10 of magnesium oxide is included here to show the strong ring of large diameter, almost filling the usable area of the film. We plan to use MgO as an internal standard, since this ring falls outside the strong rings from organics.

Figure 6 shows the result of successive dilutions of isopropyl jade green (IPJG) and aspirin with corn starch. Starch was used as a diluent, since starches and celluloses do not form crystals in the ordinary sense. However, our starch does exhibit a simple pattern (see No. 29 of Fig. 7). The first group of patterns, Nos. 13 through 18, are a series of IPJG dilutions. The first pattern is from pure IPJG. The second pattern is half IPJG and half MgO. No. 15 is 25% IPJG, 25% MgO, and 50% starch. Note that the broad inner starch ring is visible. In the other dilutions, 10%, 1%, and 1/2%, the IPJG and MgO patterns fade out, leaving only the starch pattern in the last print. The negatives show more detail than is possible to present on these prints. Further, the negatives will have to be scanned by a densitometer to bring out all details. The second group of Figure 6, Nos. 19 through 24, are from aspirin. No. 19 is pure aspirin. The series of dilutions is the same as for IPJG. Here again much detail is lost by the printing.

The first row of Figure 7 are patterns from hemin dilutions. No. 25 is 50% hemin and 50% MgO. No. 26 is 25% hemin, 25% MgO, and 50% starch. The others are 10% and 1% hemin plus MgO in starch. No. 29 is pure starch. Nos. 30, 31, and 32 are 25%, 10%, and 1% sulfaguanidine with an equal amount of MgO in starch. The last row is a series of uric acid patterns, beginning with 50% uric acid in starch, No. 33. The last three are dilutions of uric acid, the same as the hemin and sulfaguanidine above.

The amount of sample held in one of the sample washers is extremely small. A cylinder 0.6 mm in diameter by 0.6 mm long has a volume of 0.17×10^{-3} cc. In other words, this washer would hold 170 micrograms of material of unit density. Since the x-ray beam is only 0.35 mm in diameter, the diffraction pattern is produced by about 100 micrograms of sample. Hence, a 1% sample would amount only to about one microgram.

Conclusions

It is possible to obtain a recognizable diffraction pattern from a 10% sample or about 10 micrograms. Densitometric measurement of the diffraction patterns on the film should provide a means of recognizing one microgram or less of sample. Further work will be directed towards a better diluent for suspending the sample, towards better methods of placing microgram samples in the most intense portion of the x-ray beam, and towards the proper positioning of a single speck of material to produce a recognizable diffraction pattern.

Sincerely,

George

Enclosures

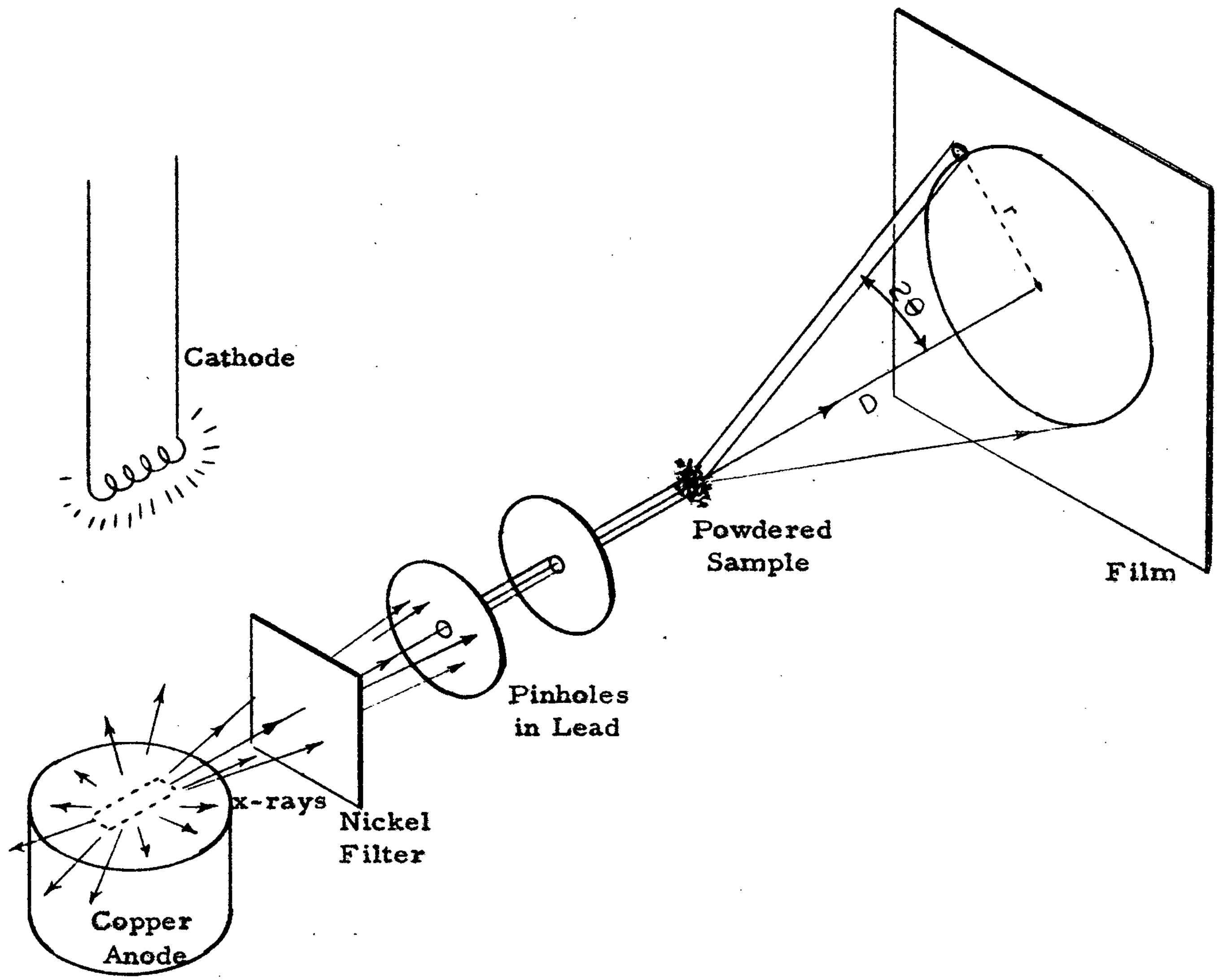

FIGURE 1. PRODUCTION OF DIFFRACTION PATTERNS BY POWDERED SAMPLES

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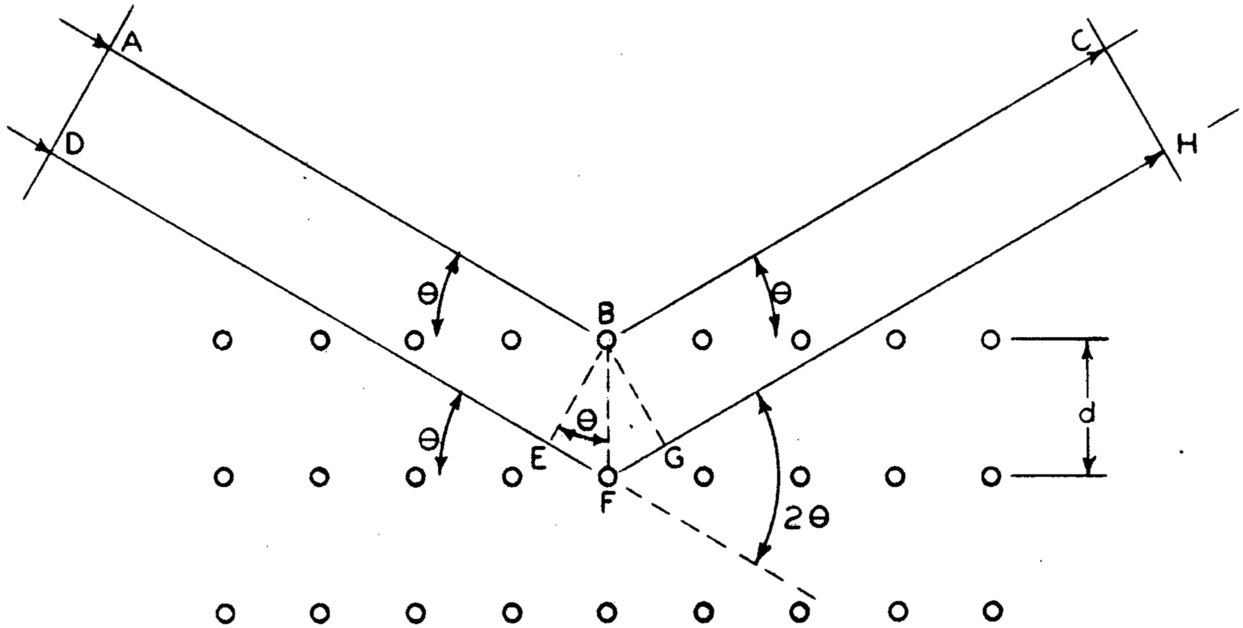


FIGURE 2. DIFFRACTION OF X-RAYS BY ATOMS IN A CRYSTAL LATTICE - BRAGG'S LAW

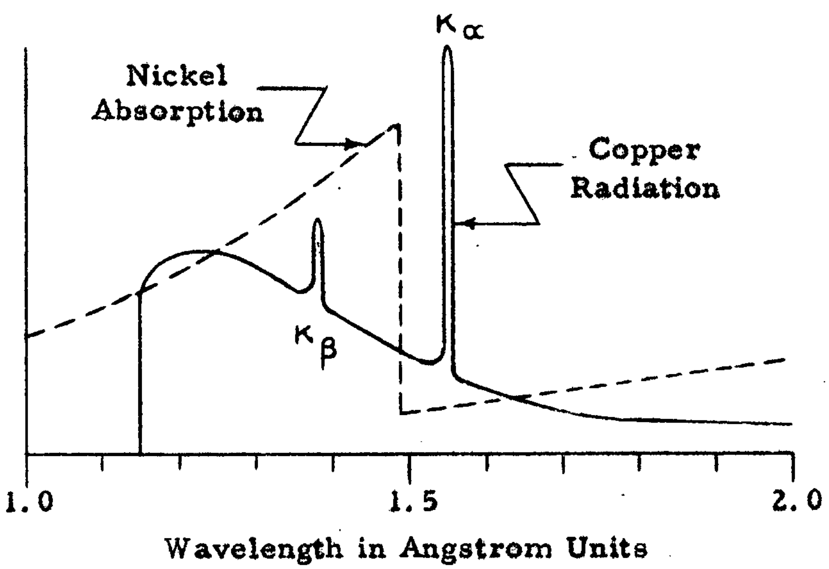
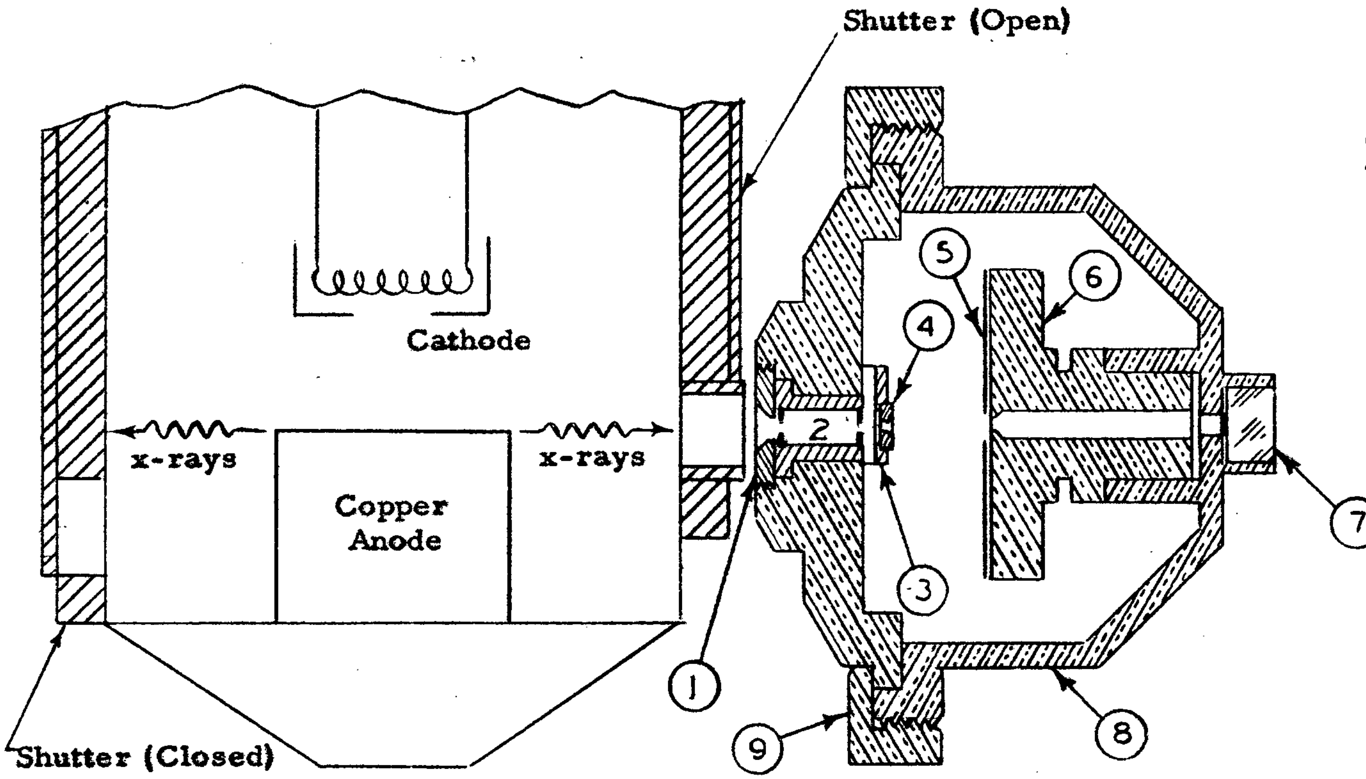


FIGURE 3. FILTERED RADIATION. CHARACTERISTIC COPPER RADIATION AND NICKEL ABSORPTION. RELATIVE INTENSITY AND ABSORPTION VERSUS WAVELENGTH.
(Note: Intensity and absorption are not to scale.)



1. Retainer
2. Pinhole collimator
3. Sample support
4. Sample washer
5. Film
6. Film support
7. Fluorescent screen and lead glass
8. Camera body
9. Clamping ring

G. E. Type CA-7 X-ray Tube

Philips Micro Camera No. 52055

FIGURE 4. DETAILS OF DIFFRACTION MICRO CAMERA IN POSITION NEXT TO THE X-RAY TUBE

FIGURE 5. TWELVE PURE COMPOUNDS

1. Sulfaguanidine.

2. Uric acid.

3. Hemin. (Note the spots from large granules. When this compound was ground finer, the diffraction rings disappeared.)

4. Disodium calcium ethylene diamine tetraacetate (EDTA).

5. Carbanthrene violet.*

6. Isopropyl jade green.

7. Disodium zinc EDTA. (Note the spots indicating large granules. The heavily exposed region in the center is due to the zinc. An exposure of four hours was required.)

8. Disodium EDTA. The few spots scattered along the rings indicate that powder is almost uniform.

9. Disodium magnesium EDTA.

10. Magnesium oxide.* This compound is included here, since it is used as an internal standard.

11. 8-Hydroxyquinoline.

12. Dimethylglyoxime.

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*Made on Ilford x-ray industrial G film. Exposure time: 15 minutes.

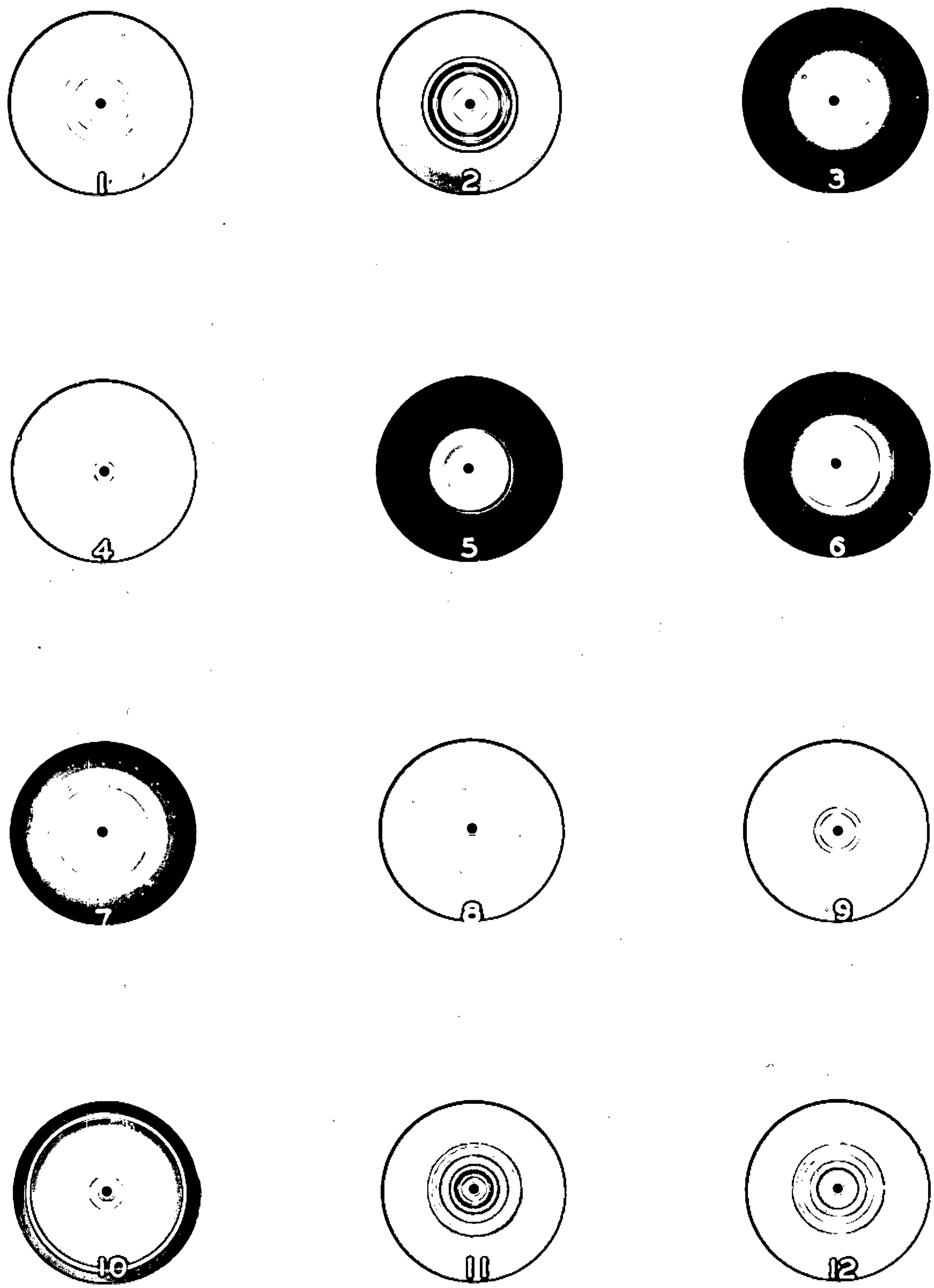
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FIGURE 6. ISOPROPYL JADE GREEN AND ASPIRIN AT VARIOUS DILUTIONS

Nos. 13 through 18: Isopropyl Jade Green

13. Pure IPJG.
14. 50% IPJG - 50% MgO.
15. 25% IPJG - 25% MgO - balance starch.
16. 10% IPJG - 10% MgO - balance starch.
17. 1% IPJG - 1% MgO - balance starch.
18. 1/2% IPJG - 1/2% MgO - balance starch.

Nos. 19 through 24: Aspirin

19. Pure aspirin.
20. 50% aspirin - 50% MgO - balance starch.
21. 25% aspirin - 25% MgO - balance starch.
22. 10% aspirin - 10% MgO - balance starch.
23. 1% aspirin - 1% MgO - balance starch.
24. 1/2% aspirin - 1/2% MgO - balance starch.

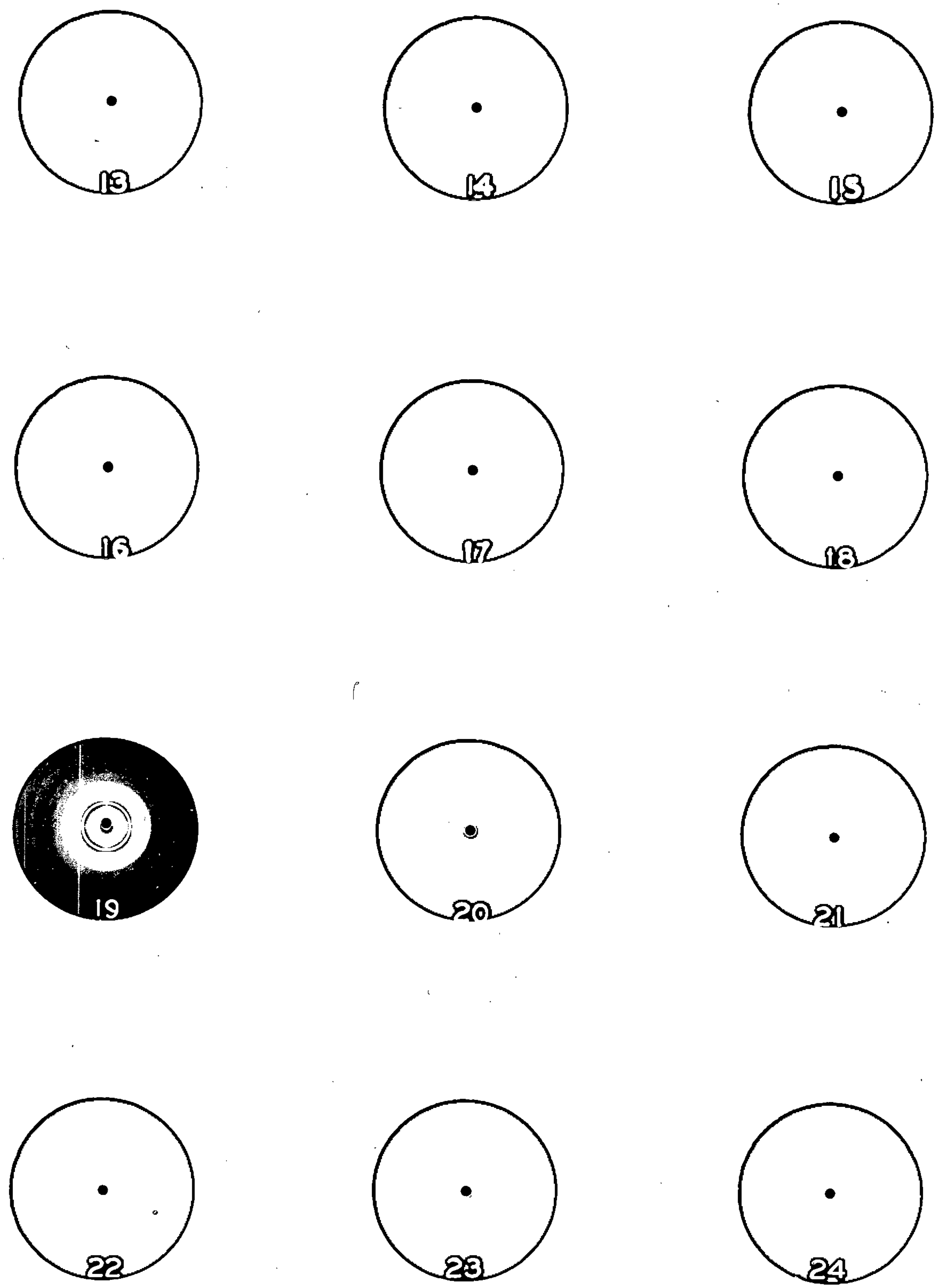
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FIGURE 7. VARIOUS COMPOUNDS AND DILUTIONS

25. 50% hemin - 50% MgO.

26. 25% hemin - 25% MgO - balance starch.

27. 10% hemin - 10% MgO - balance starch.

28. 1T hemin - 1% MgO - balance starch.

29. Corn starch.

30. 25% sulfaguanidine - 25% MgO - balance starch.

31. 10% sulfaguanidine - 10% MgO - balance starch.

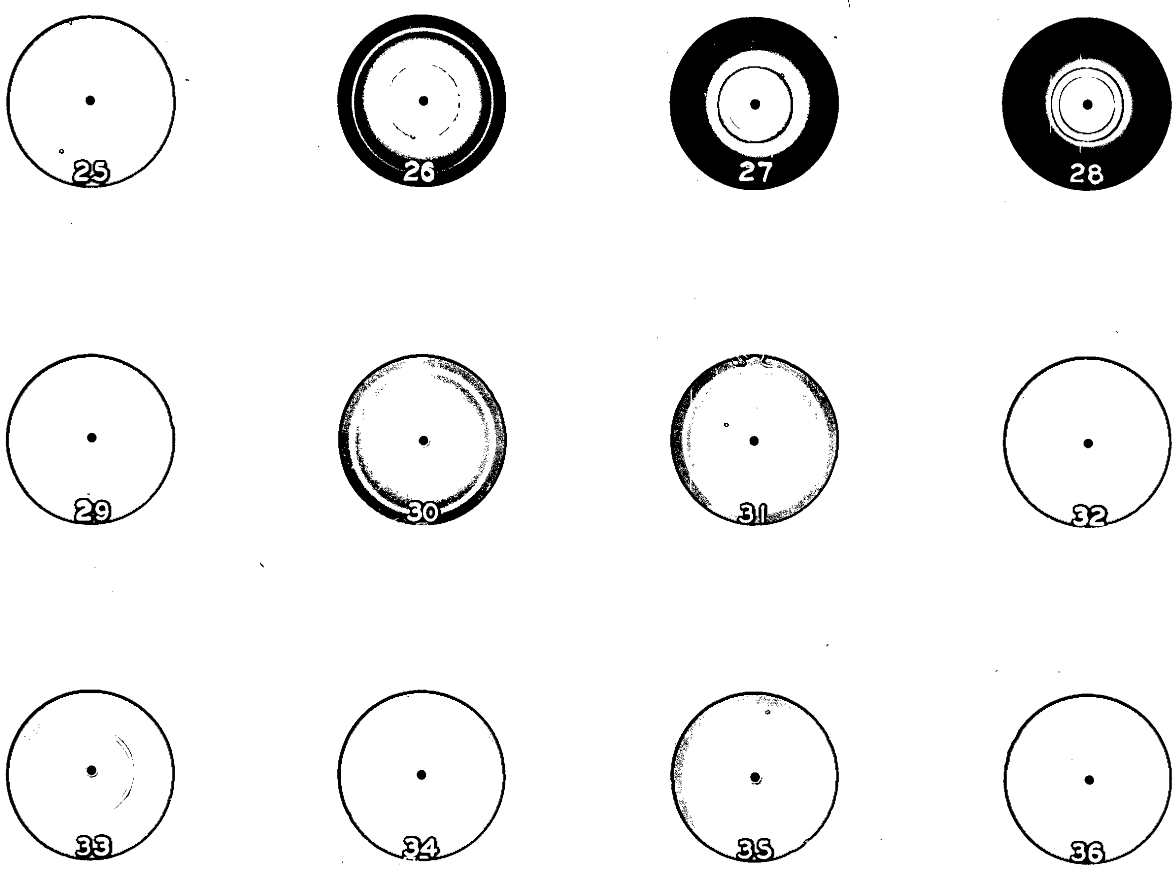
32. 1% sulfaguanidine - 1% MgO - balance starch.

33. 50% uric acid - 50% starch.

34. 25% uric acid - 25% MgO - balance starch.

35. 10% uric acid - 10% MgO - balance starch.

36. 1% uric acid - 1% MgO - balance starch.



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